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# X-RAY DIFFRACTION PHASE ANALYSIS OF PROCESS

by

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16. ABSTRACT The paper describes the application of x-ray diffraction (XRD) analysis to several samples which show the information available from the technique. X-ray fluorescence (XRF) spectrometry was used for the elemental analysis because it provides very complete information with minimal sample preparation and analysis time. Two samples were analyzed which illustrate the difference between the final products obtained from the incineration of a waste crankcase oil sample by pot vaporization and air atomization. Also analyzed were particulate samples from two commercial waste incinerators, as well as three samples from lead and copper smelters. Study results indicate that XRD, applied with XRF, can be an effective tool for the characterization of industrial process streams. Information gained from this technique can be used for process and pollution control equipment evaluation and for by-product disposal criteria.

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| Analyzing | Spectroscopy | | 14B |
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# X-RAY DIFFRACTION PHASE ANALYSIS OF PROCESS AND POLLUTION CONTROL DEVICE SAMPLES

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## INTRODUCTION

Much attention has been directed to the analysis of process samples for potentially harmful elements. However, the chemical and physical properties of the substances are a function of the species with which they are chemically associated. Since the physical properties such as polarity, polarizability, resistivity, density, friability, and solubility depend on the compound or phase, this factor should be a primary consideration in the design and operation of emission control devices and the disposal of their by-products.

X-ray diffraction analysis (XRD) can provide the most definitive phase information of all the methods available. It is the goal of this study to demonstrate the efficacy of XRD in the characterization of actual process samples. Some interesting results from studies on crankcase oil incineration residues and ashes, smelter particulates, and composite waste incineration particulates are reported.

Waste incineration by-products can be very complex due to the variability of the waste feed streams and incinerator processes. This paper describes the application of XRD to several selected samples which demonstrate the information available from the technique. To facilitate the interpretation of the XRD data, it is desirable to have elemental analysis of the sample. In this Laboratory, X-ray fluorescence spectrometry (XRF) is used for the elemental analysis because it provides very complete information with minimal sample preparation and analysis time. The XRF elemental analysis makes it possible to reject unlikely phases

from the XRD data search and also allows a semi-quantitative interpretation of the XRD data by establishment of limits on elemental concentrations.

## EXPERIMENTAL

For XRF elemental analysis, samples on filters are analyzed without further preparation. Solid samples are ground and mixed 1:3 with an organic binder and pressed into a pellet. The samples are qualitatively scanned on a sequential wavelength dispersive spectrometer using conditions that cover the range of elements from sodium (Z=11) to uranium (Z=92) with logarithmic amplification. After the qualitative scan, each element found to be present is counted with appropriate standards. The resulting data are reduced using the Criss Fundamental Parameters XRF-11 algorithm.

For XRD phase analysis, samples on filters are analyzed without further preparation. Solid samples are ground and mounted in a bulk specimen holder if sufficient quantities are available and they hold together properly. If not, the samples are cast in a collodion film on glass slides. The samples are scanned with a diffractometer. The XRD data is then reduced using the Joint Committee on Powder Diffraction Standards (JCPDS) files. During the search, the XRF elemental analysis is used to reject unlikely phases.

## RESULTS AND CONCLUSIONS

Two samples were analyzed which illustrate the difference between the final products obtained from the incineration of a waste crankcase oil sample by pot vaporization and air atomization. Table 1 shows 58% of elements less than atomic number 11 (sodium) for the pot vaporization furnace residue. This fraction is due to cracking of the oil to form long chain polymers. XRF doesn't detect elements of $Z < 11$ but the quantity was obtained by difference. This number compared favorably with that obtained by pyrolysis which was 55%. Lead and zinc sulfide were the major residue constituents detectable by XRD. The air atomization furnace produces large amounts of lead particulates with the major XRD peaks belonging to lead bromide chloride. There were two zinc phosphate phases possible which could not be confirmed because all the XRD peaks were hidden by those of the more abundant phases.

The data for two particulate samples from commercial waste incinerators are shown in Table 2. Incinerator A shows large amounts of chlorine, sodium, and calcium. The XRD analysis showed very strong peaks for sodium chloride, indicating that its production is strongly favored in halogen material combustion. The incinerator B products were high in silicon, titanium, iron, and calcium, implying that paint materials composed a large part of its feed stream. The main XRD peaks were from silicon dioxide with some contribution

from a calcium iron silicate.

The results from the analysis of three samples from lead and copper smelters are given in Table 3. Lead sulfate was a favored phase for all three processes. The phases cadmium carbonate in the lead blast furnace and arsenic trioxide in the copper electrostatic precipitator (ESP) are also of environmental significance. In the latter process, arsenic trioxide is seen to be the major constituent.

X-ray diffraction phase analysis, applied with X-ray fluorescence elemental analysis, can be an effective tool for the characterization of industrial process streams. Information gained from this technique can be used for process and pollution control equipment evaluation and for by-product disposal criteria.

Table 1. Analysis of Crankcase Oil Incineration Samples

| Element (XRF) | Pot Vaporization Residue | Air Atomization Particulate |
|---|---|---|
| Z <11 | 58.76% | 8.22% |
| Magnesium | 0.23 | 1.82 |
| Aluminum | 0.20 | 0.72 |
| Silicon | 0.20 | 0.37 |
| Phosphorous | 4.11 | 8.32 |
| Sulfur | 4.49 | 2.07 |
| Chlorine | 0.35 | 3.64 |
| Potassium | 0.13 | 0.26 |
| Calcium | 3.71 | 6.51 |
| Iron | 1.28 | 2.18 |
| Nickel | 0.015 | 0.031 |
| Copper | 0.23 | 0.68 |
| Zinc | 4.44 | 11.24 |
| Bromine | 0.61 | 5.84 |
| Strontium | 0.39 | 0.53 |
| Molybdenum | 0.11 | 0.23 |
| Barium | 0.35 | 0.61 |
| Lead | 18.88 | 46.73 |
| Phases from XRD (JCPDS Ref.) | PbS (5-592)<br>ZnS (5-566)<br>$Pb_9(PO_4)_6$ (26-903) | PbBrCl (24-1088)<br>$Pb_3P_4O_{13}$ (12-18)<br>$PbSO_4$ (5-577) |

Table 2. Analysis of Commercial Incinerator Effluents

| Element | Incinerator A Particulate | Incinerator B Ash |
|---|---|---|
| Sodium | 23.2% | 1.5% |
| Magnesium | 0.25 | 2.2 |
| Aluminum | 1.7 | 3.5 |
| Silicon | 5.8 | 13.0 |
| Phosphorous | 8.2 | 0.42 |
| Sulfur | 4.0 | 0.61 |
| Chlorine | 25.0 | 2.0 |
| Potassium | 3.5 | 0.85 |
| Calcium | 14.0 | 9.2 |
| Titanium | 6.4 | 9.2 |
| Iron | 1.5 | 6.1 |
| Nickel | 0.47 | 0.38 |
| Copper | 0.47 | 0.072 |
| Zinc | 2.0 | 0.075 |
| Bromine | 0.43 | 0.074 |
| Tin | 0.05 | 0.0 |
| Lead | 2.6 | 0.056 |
| Phases from XRD (JCPDS Ref.) | NaCl (5-628)<br>KPbCl (27-1364) | $SiO_2$ (5-494)<br>$Ca(Mg,Fe)Si_2O_6$ (24-203) |

Table 3. Analysis of Smelter Samples

| Element (XRF) | Lead Blast Furnace | Copper Roaster | Copper ESP |
|---|---|---|---|
| Silicon | 1.0% | 3.4% | 1.1% |
| Sulfur | 2.5 | 5.1 | 5.7 |
| Iron | 0.23 | 5.4 | 4.3 |
| Copper | 1.5 | 2.3 | 2.2 |
| Zinc | 0.03 | 3.6 | 2.0 |
| Arsenic | 0.6 | 1.0 | 41.0 |
| Cadmium | 8.46 | 6.4 | 0.3 |
| Tin | 2.2 | 2.2 | 0.0 |
| Antimony | 0.0 | 0.0 | 2.3 |
| Lead | 18.7 | 7.5 | 10.0 |
| Phases from XRD (JCPDS Ref) | $CdCO_3$(8-456)<br>$PbSO_4$(5-577)<br>$SiO_2$ (11-695)<br>$Pb(SO_4)O$(18-702) | $PbSO_4$(5-577)<br>$SiO_2$ (14-654)<br>CuO (5-661)<br>$Fe_2O_3$(24-81) | $As_2O_3$(4-566)<br>$PbSO_4$(5-577) |